HySCORE

Hydrogen Storage Characterization and Optimization Research Effort

Martin Head-Gordon and Jeffrey R. Long

Materials Sciences Division
Lawrence Berkeley National Laboratory
June 7, 2017

Project ID #: ST133

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

HySCORE

Timeline*

Project Start: 10/1/2015
End: Project continuation determined by DOE. Currently scheduled through 9/30/18
(*previously a component of NREL's materials development program and supported annually since 2006)

Budget

Total Team Budget: (HySCORE): $8.2M
Federal Share:
NREL: $2.6M
LBNL: $2.4M
PNNL: $2.4M
NIST: $0.8M
LBNL Funds Spent: ~$1.67M
(Estimated as of 3/31/17)

Barriers addressed

General:
A. Cost, B. Weight and Volume, C. Efficiency,
E. Refueling Time
Reversible Solid-State Material:
M. Hydrogen Capacity and Reversibility
N. Understanding of Hydrogen Physi- and Chemisorption
O. Test Protocols and Evaluation Facilities

Partners/Collaborators

NIST – Craig Brown, Terry Udovic
PNNL – Tom Autrey, Mark Bowden
NREL – Tom Gennett
HyMARC – SNL, LLNL, LBNL
LLNL, USA – Brandon Wood
H_2ST^2, USA – Hydrogen Storage Tech Team

Relevance

HySCORE

Project objectives

- Develop *in situ* infrared spectroscopy as a tool for characterizing emerging H_2 storage materials that may allow for a driving range greater than 300 miles
  - *Double* hydrogen storage energy density (increase from 25g/L to 50 g/L)
- Materials sought with the potential for meeting the DOE targets of reversible uptake
- Validate new concepts for H_2 storage mechanisms in adsorbents
- Provide accurate computational modeling for H_2 adsorbed in porous materials

This reporting period

- Research and development of metal-organic framework materials with high volumetric and gravimetric H_2 capacities (Barrier A - E).
- DRIFTS characterization (Barrier N,O)

Role of LBNL within the Effort

HySCORE

Hydrogen Storage Characterization and Optimization Research Effort

Researchers at NREL, LBNL, PNNL, and NIST are tasked with supporting the DoE Hydrogen Storage Program through validation of:

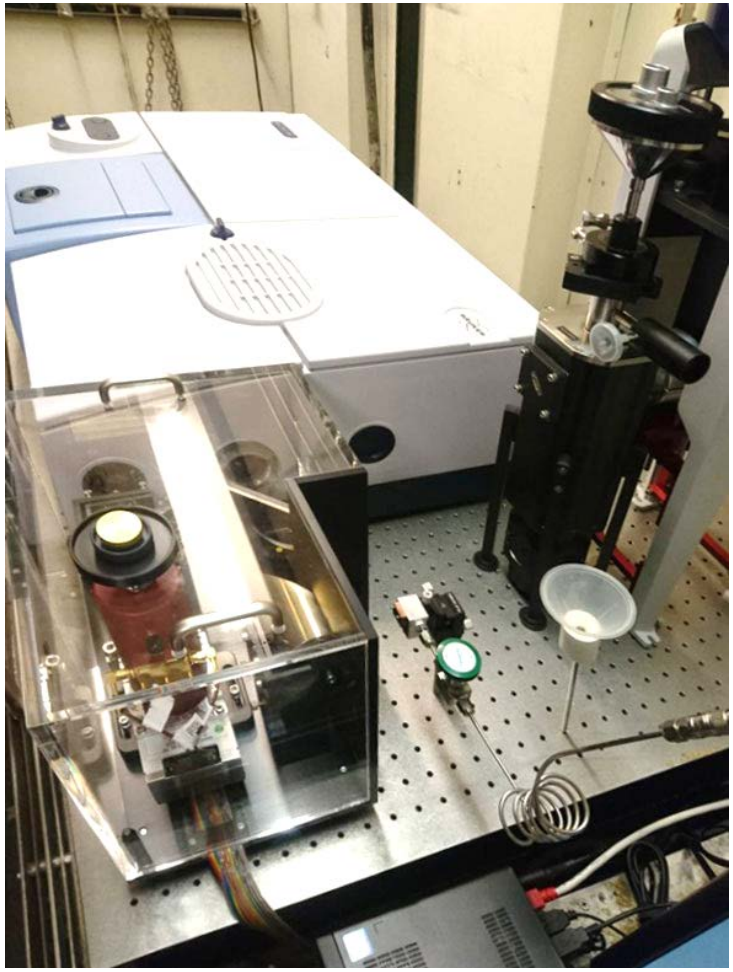
1) Properties of emerging hydrogen storage materials
2) New concepts for hydrogen storage mechanisms
3) Computational methods for predicting hydrogen storage properties

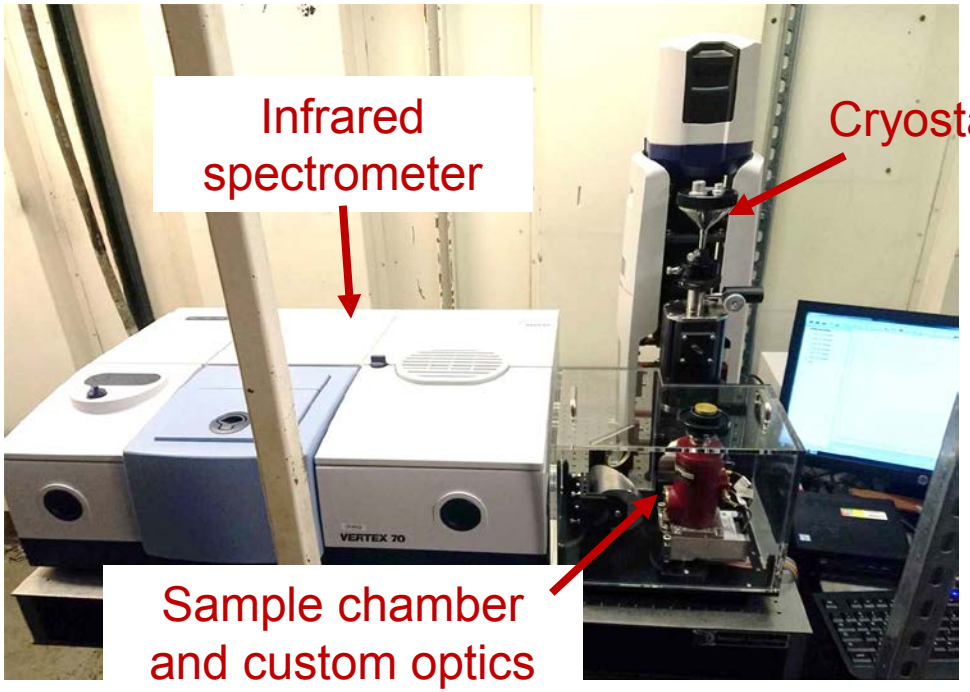
LBNL:

1) IR spectroscopy with precise H_2 dosing at T = 10-300 K, $P \leq 100$ bar
2) Mechanistic validation:
   - Can exposed cations in adsorbents reach target of $\Delta H = -15$ kJ/mol?
   - Is it possible to adsorb two, three, or four H_2 per metal cation?
3) Accurate modeling of H_2 adsorbed within porous materials

Accomplishments: LBNL Core Capability
In Situ Infrared Spectroscopy

HySCORE

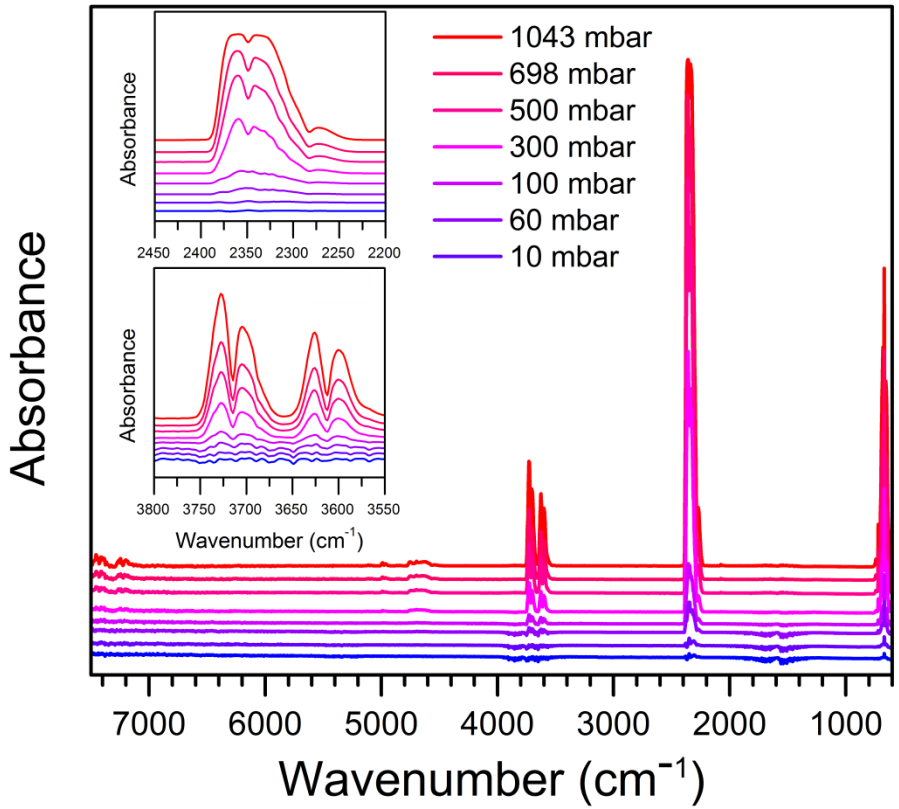


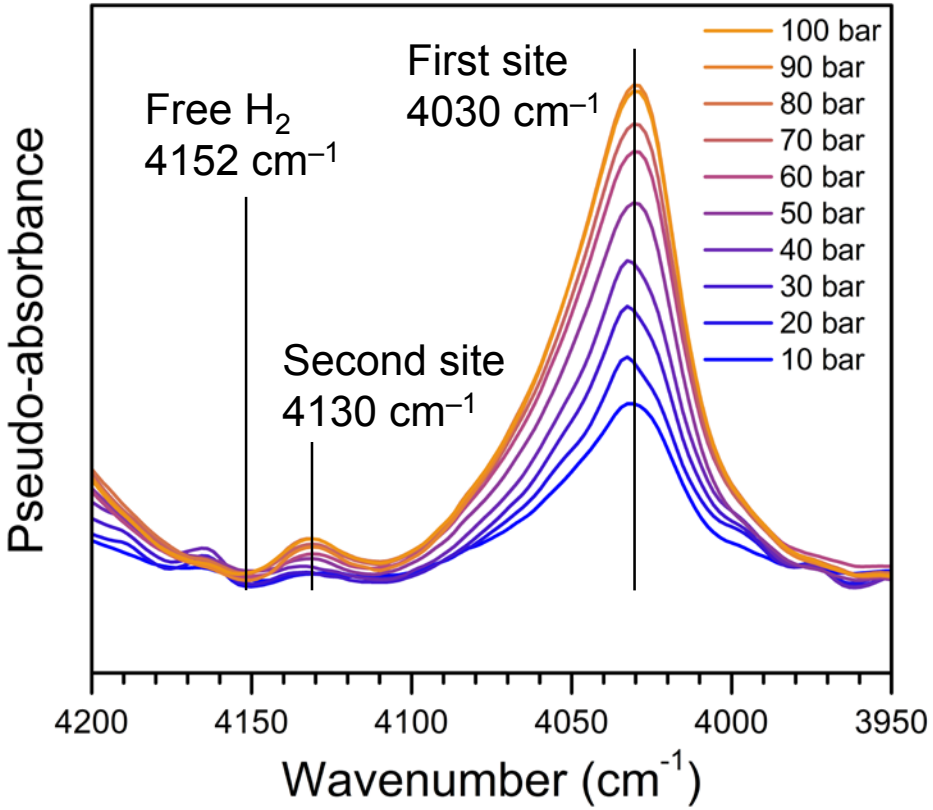


- All components of the *in situ* infrared spectrometer were ordered and installed in this reporting period
- Ultimate capabilities of the instrument:
  - 15 − 373 K temperature range
  - 0 − 100 bar pressure range

Henry Jiang

Accomplishments: High-Pressure *in situ* Infrared Spectra





- (Left) CO_2 spectra collected on the *in situ* gas dosing infrared spectrometer in an empty sample cell, showing increasing signal with increasing gas pressure at room temperature.
- (Right) Spectrum of H_2 bound in Ni_2(*m*-dobdc) between 10 and 100 bar at 298 K
- Spectra matches very well with literature spectra

Relevance: DOE 2020 H_2 Storage System Targets

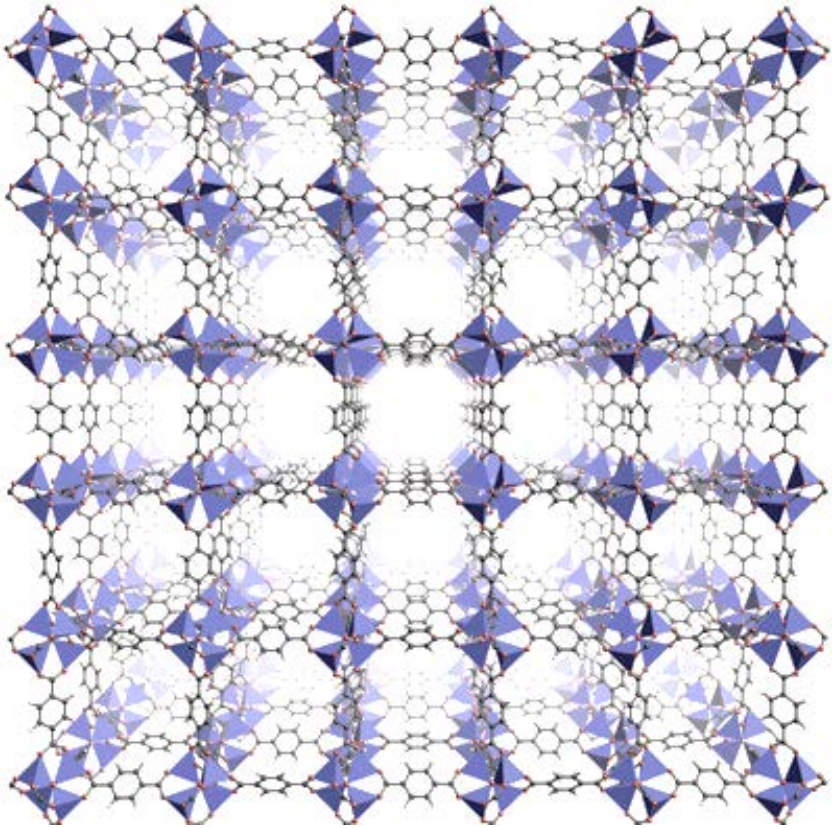
HySCORE

Gravimetric capacity	5.5 wt. % H_2
Volumetric capacity	40 g H_2/L
Operating ambient temperature	–40 to 60 °C
Refueling rate	1.67 kg H_2/min
Cycle life	1500 cycles
Cost	$333 per kg H_2
Maximum pressure	100 bar (project goal)

http://energy.gov/sites/prod/files/2015/05/f22/fcto_myrdd_storage.pdf

Approach: Metal-Organic Frameworks

HySCORE



$Zn_4O(1,4\text{-benzenedicarboxylate})_3$

MOF-5

BET surface areas up to 7100 m^2/g

Densities as low as 0.13 g/cm^3

Tunable pore sizes up to 10 nm

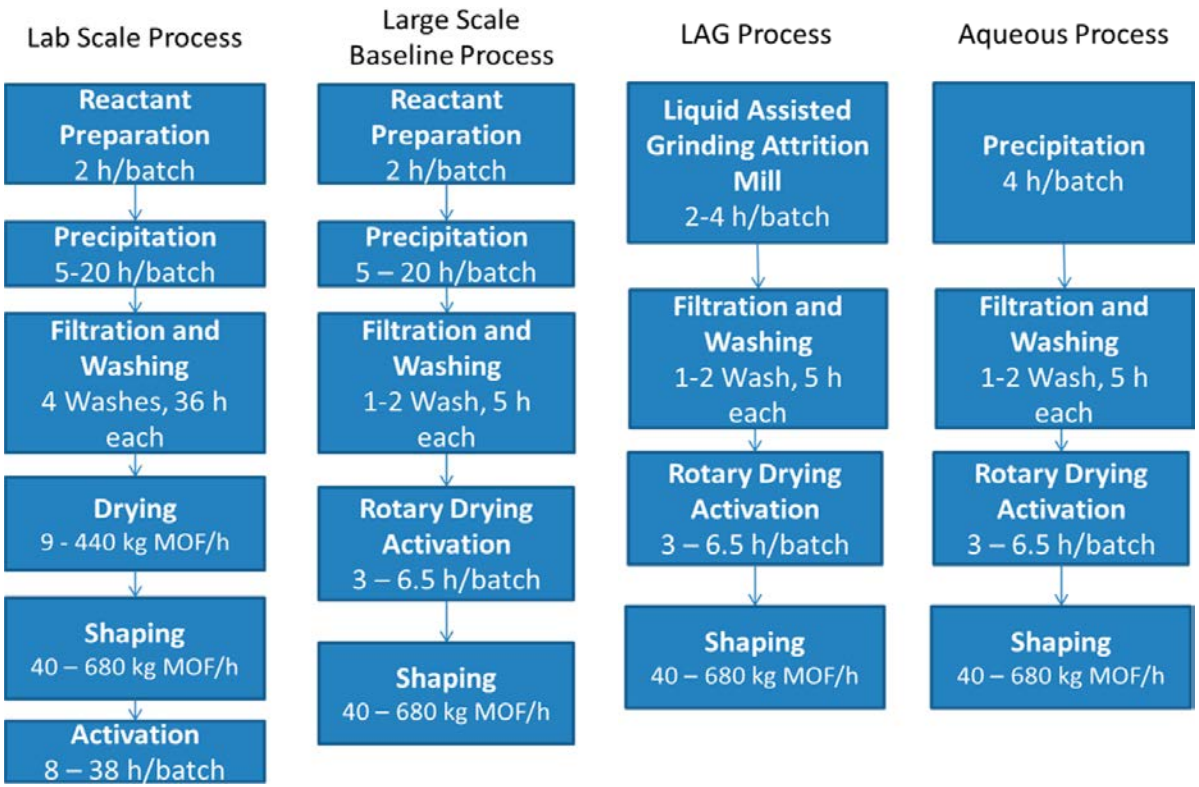
Channels connected in 1-, 2-, or 3-D

Internal surface can be functionalized

Can these high-surface area materials be used for hydrogen storage at ambient temperatures?

Yaghi *et al. Nature* **2003**, *423*, 705
Kitagawa *et al. Angew. Chem., Int. Ed.* **2004**, *43*, 2334
Férey *Chem. Soc. Rev.* **2008**, *37*, 191

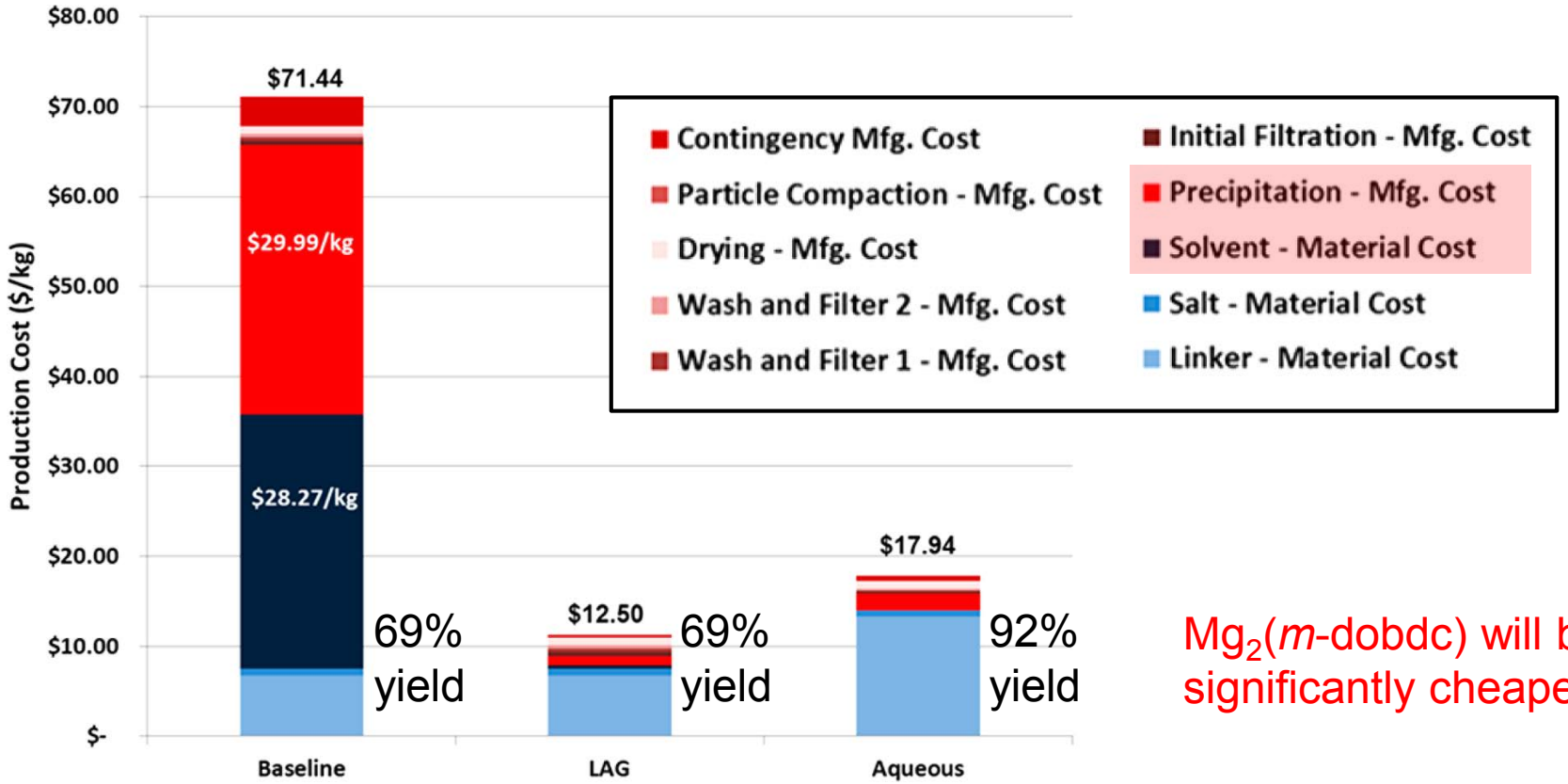
Accomplishments: Techno-Economic Analysis of MOF Production



- A techno-economic analysis of a variety of MOFs, including Mg_2(dobdc), was undertaken to understand how the cost of these materials can be reduced at scale
- Block flow diagrams show the steps for various MOF production processes
- Technology transfer: study of industrial production and ongoing study in MOF scaleup

DeSantis, Mason, James, Houchins, Long, Veenstra *Energy Fuels* **2017**, *31*, 2024

Accomplishments: Techno-Economic Analysis of Mg_2(dobdc) Production



Mg_2(*m*-dobdc) will be significantly cheaper!

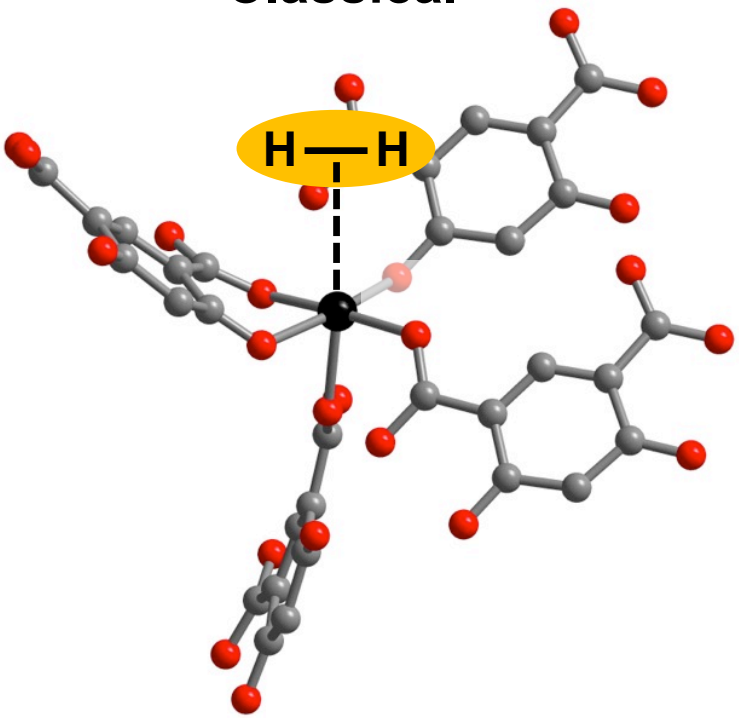
- Largest costs for Mg_2(dobdc) production are precipitation (manufacturing) and solvent (material) costs, in addition to low yield.
- Liquid-assisted grinding (LAG) and aqueous synthesis both substantially decrease cost.

DeSantis, Mason, James, Houchins, Long, Veenstra *Energy Fuels* **2017**, *31*, 2024.

Approach: Binding Multiple H_2 Molecules per Metal Cation

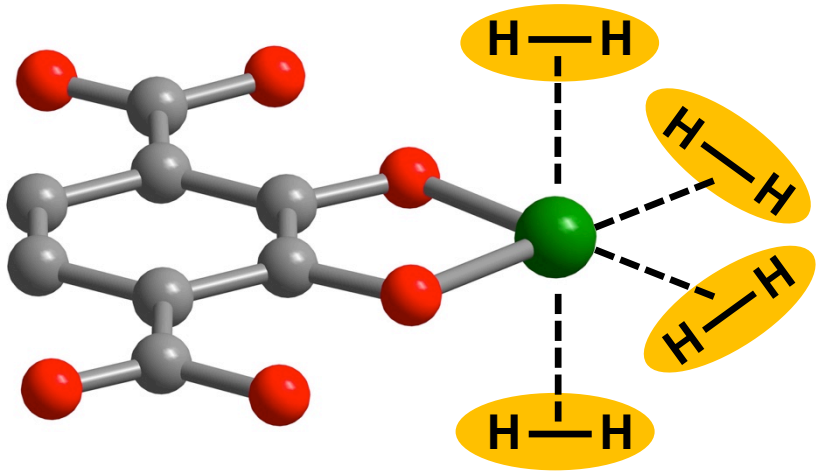
HySCORE

Classical



1 H_2 per metal cation

Next-Generation

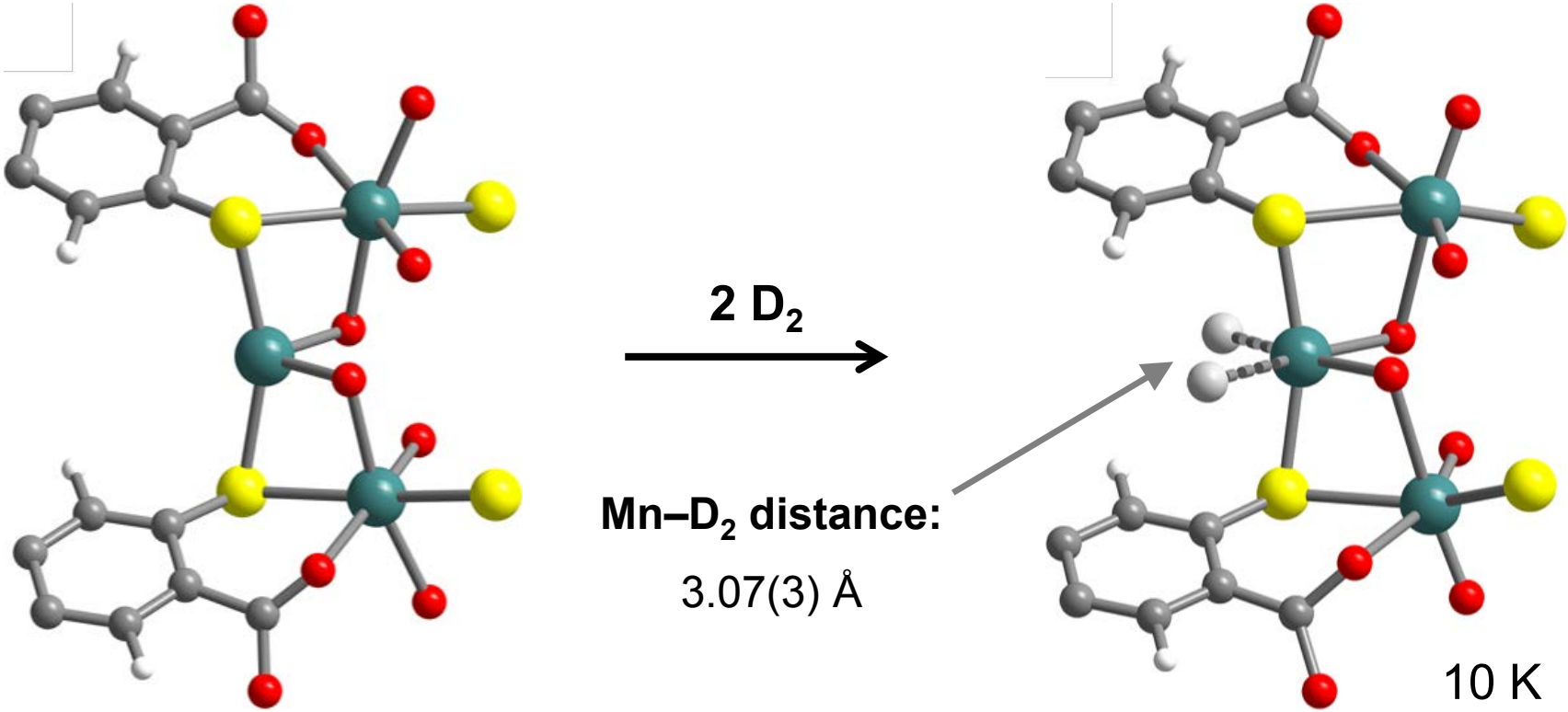


4 or 5 H_2 per metal cation

Volumetric capacity can be substantially increased while maintaining or increasing binding strength.

Previous Work: D_2 Adsorption in Mn_2(dsbdc)

HySCORE

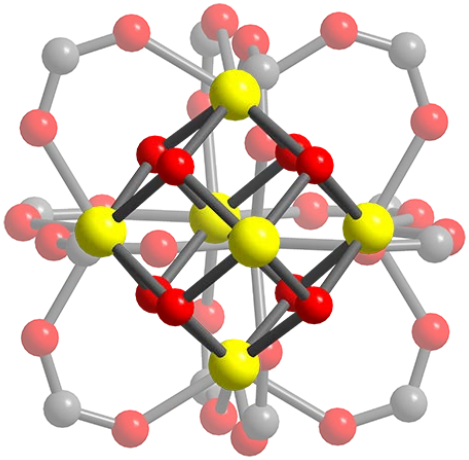


- First demonstration of 2 H_2 molecules adsorbed at a single metal center
- Proof of principle supporting future work
- H_2 binding enthalpy (–5.6 kJ/mol) must be increased for higher capacity

Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long *Chem. Commun.* **2016**, *52*, 8351

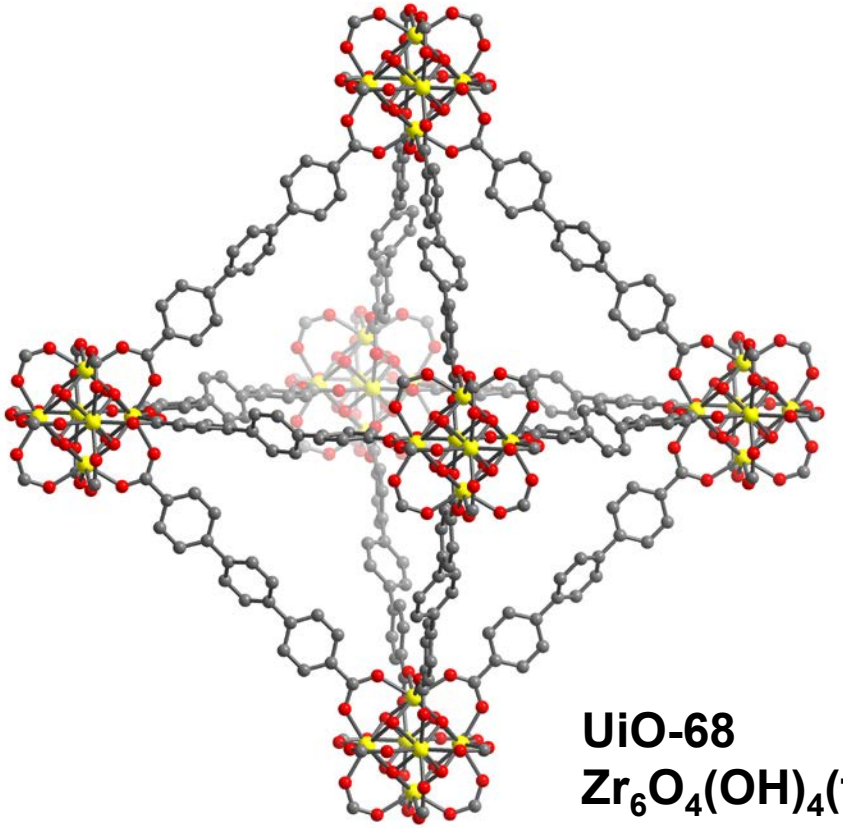
Approach: Metallation of $Zr_6O_4(OH)_4(tpdc)_6$

HySCORE



$Zr_6O_4(OH)_4(CO_2)_{12}$ cluster

$tpdc^{2-}$



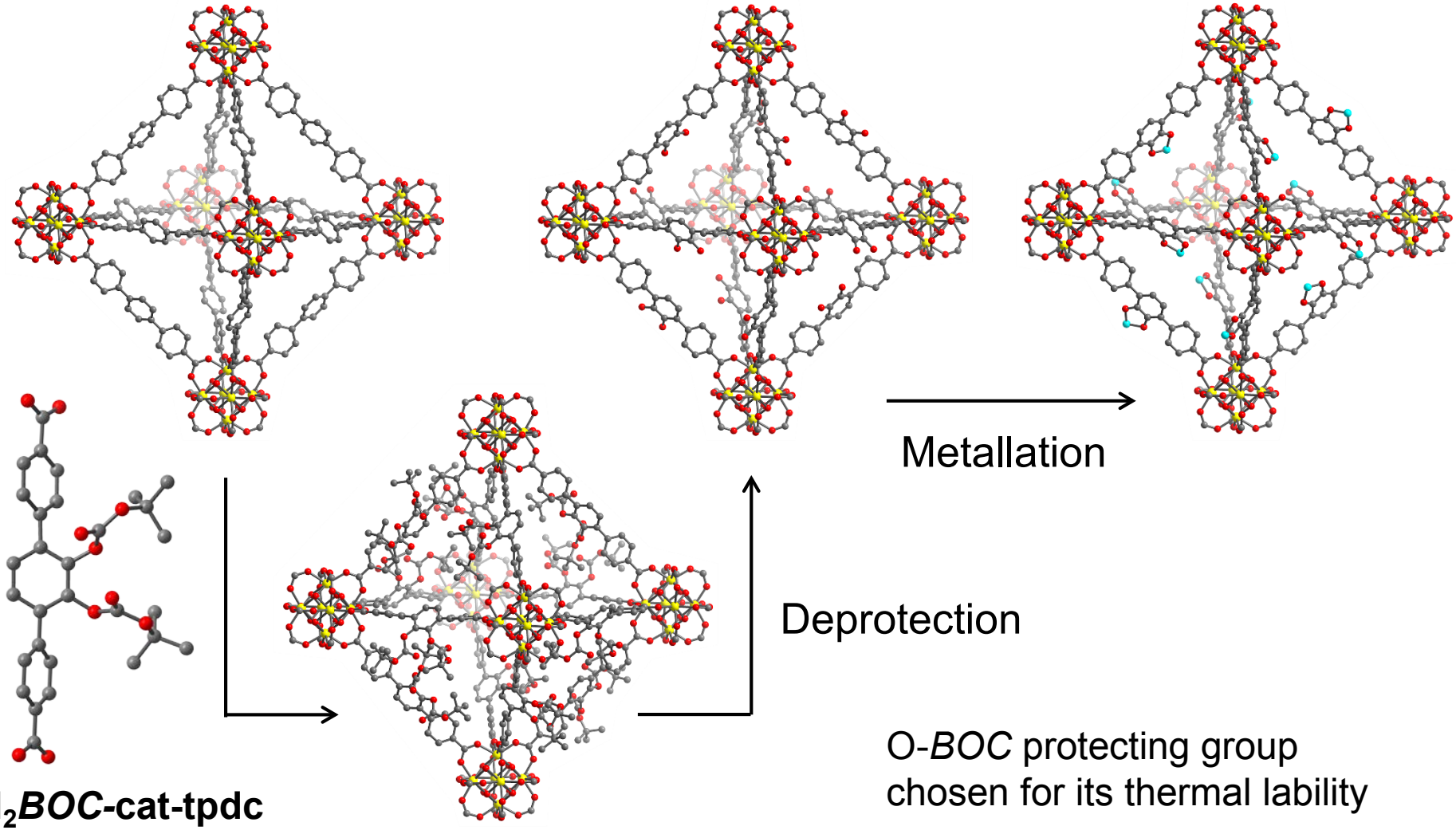
UiO-68
$Zr_6O_4(OH)_4(tpdc)_6$

- Robust platform for functionalization
- Large pores facilitate post-synthetic modification

Cavka, Jakobsen, Olsbye, Guillou, Lamberti, Bordiga, Lillerud *J. Am. Chem. Soc.* **2008**, *130*, 13850.

Approach: BOC Protecting Group for Framework Synthesis and Deprotection

HySCORE

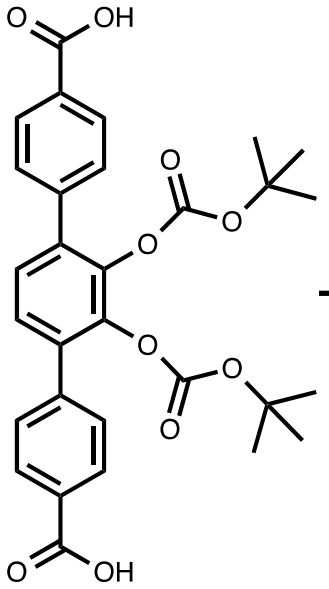


H_2*BOC*-cat-tpdc

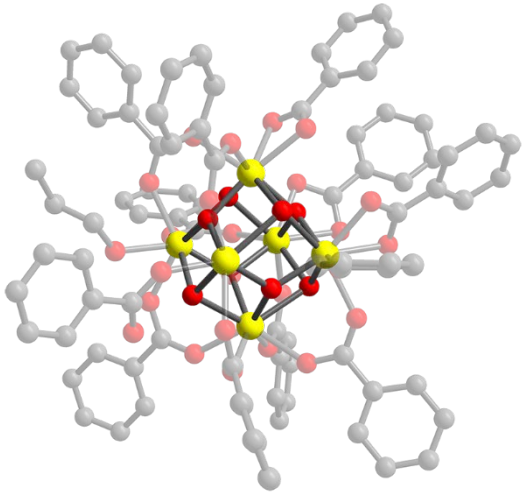
O-*BOC* protecting group chosen for its thermal lability

Accomplishments: Synthesis of *BOC*-cat-UiO-68

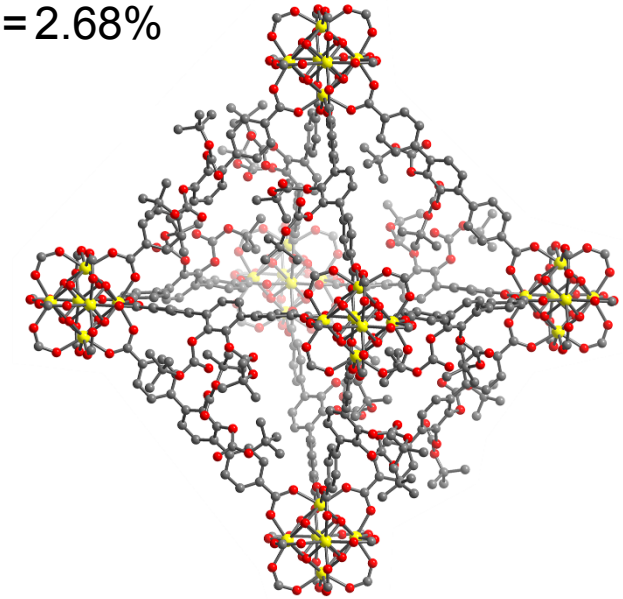
HySCORE



+



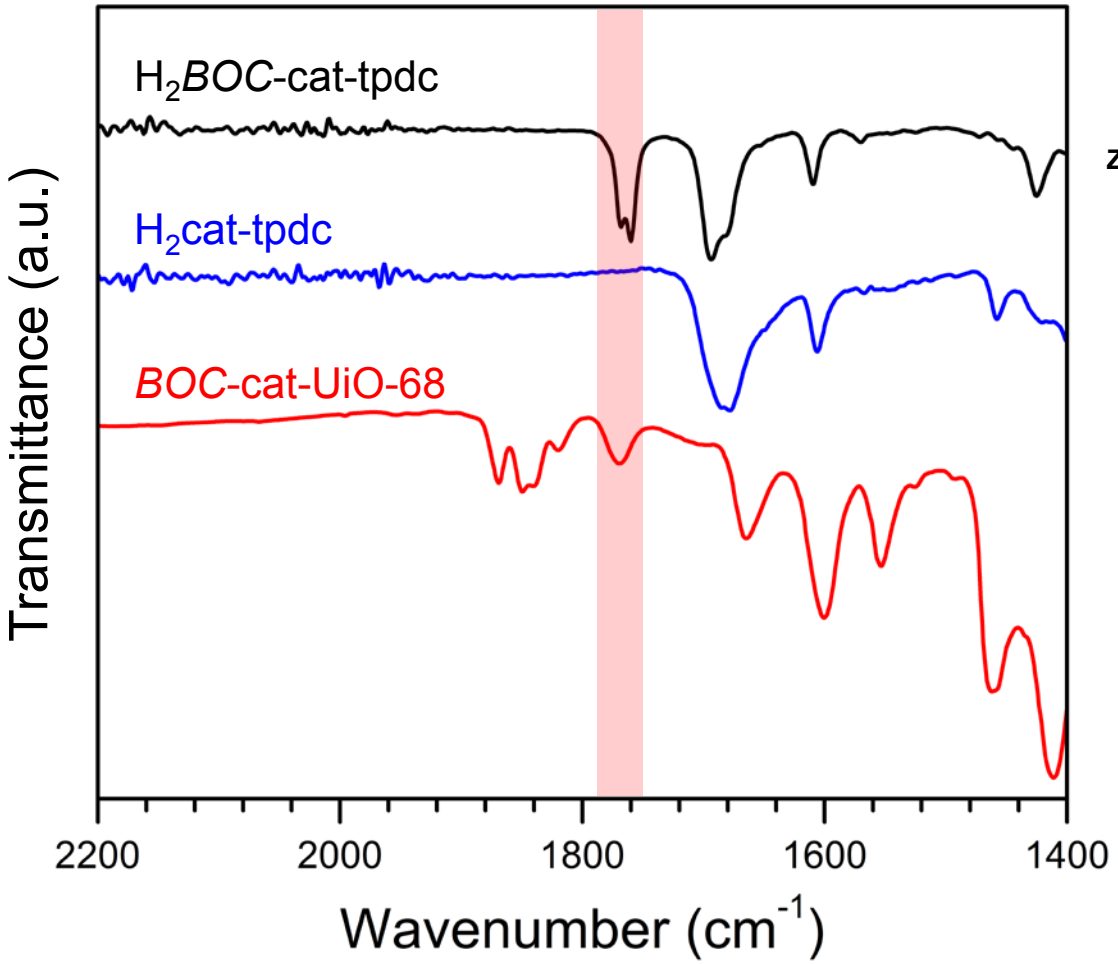
Cubic, $Fm\bar{3}m$
a = 32.88(1) Å
R_{wp} = 2.68%

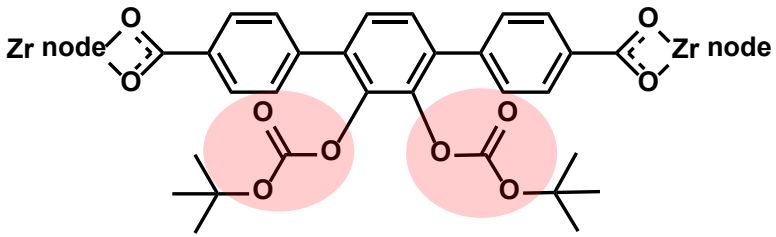


H_2*BOC*-cat-tpdc **$Zr_6O_4(OH)_4(C_6H_5COO)_{12}$(*n*Pr-OH)** ***BOC*-cat-UiO-68**

Decreased reaction temperature and the use of a pre-formed cluster were found to be necessary to obtain the intended crystalline MOF product.

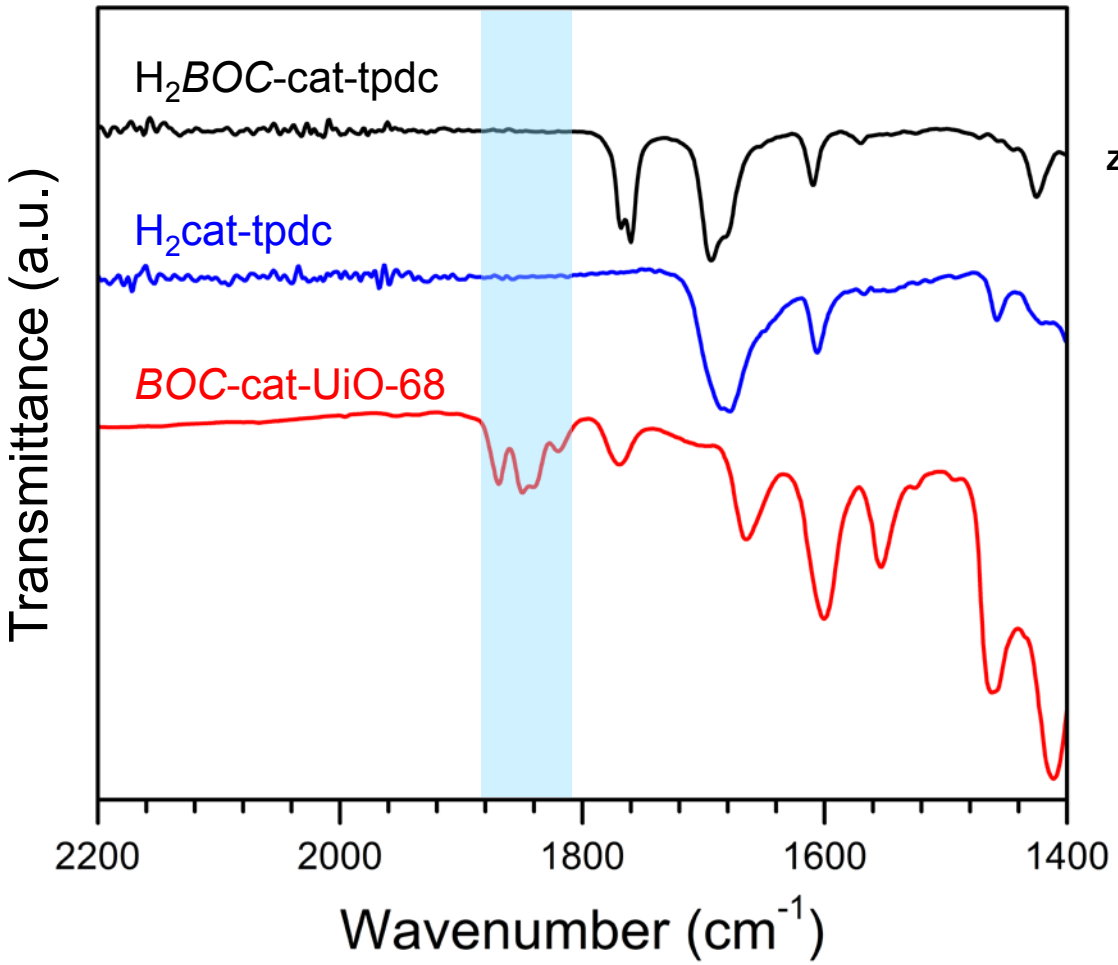
Accomplishments: Presence of BOC Protecting Groups

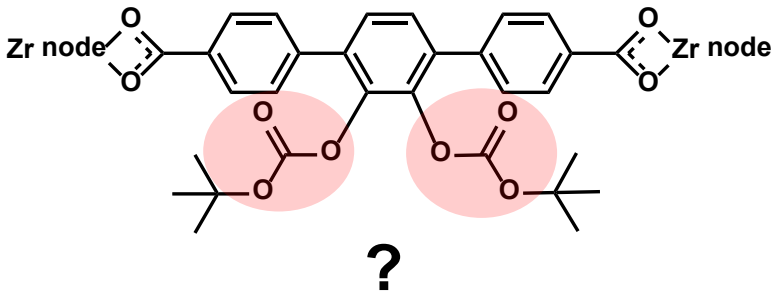




BOC protecting group is seen to disappear by infrared spectroscopy when deprotecting the ligand but can be seen in the protected MOF

Accomplishments: Unknown IR Peaks in the *BOC*-Protected MOF

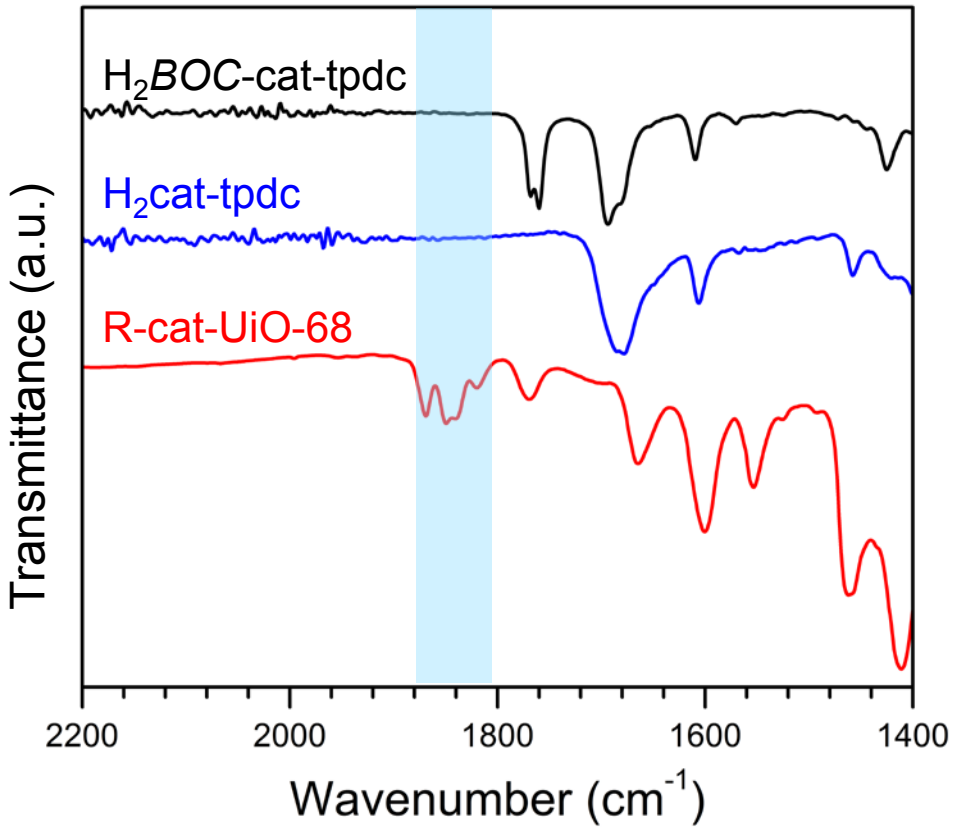


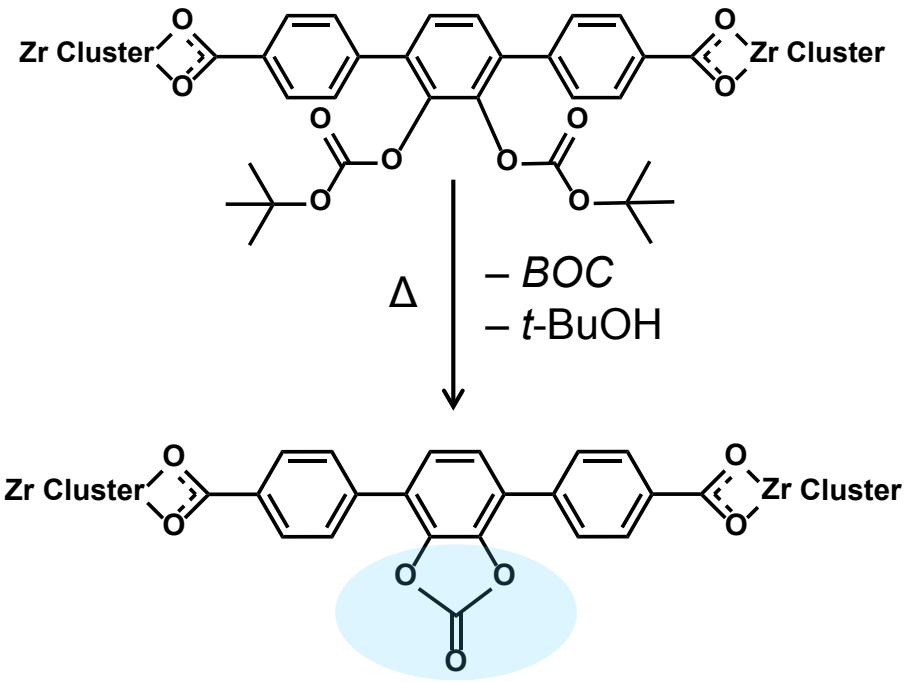


?

However, the appearance of several stretches in the *BOC*-protected MOF are of unknown origin.

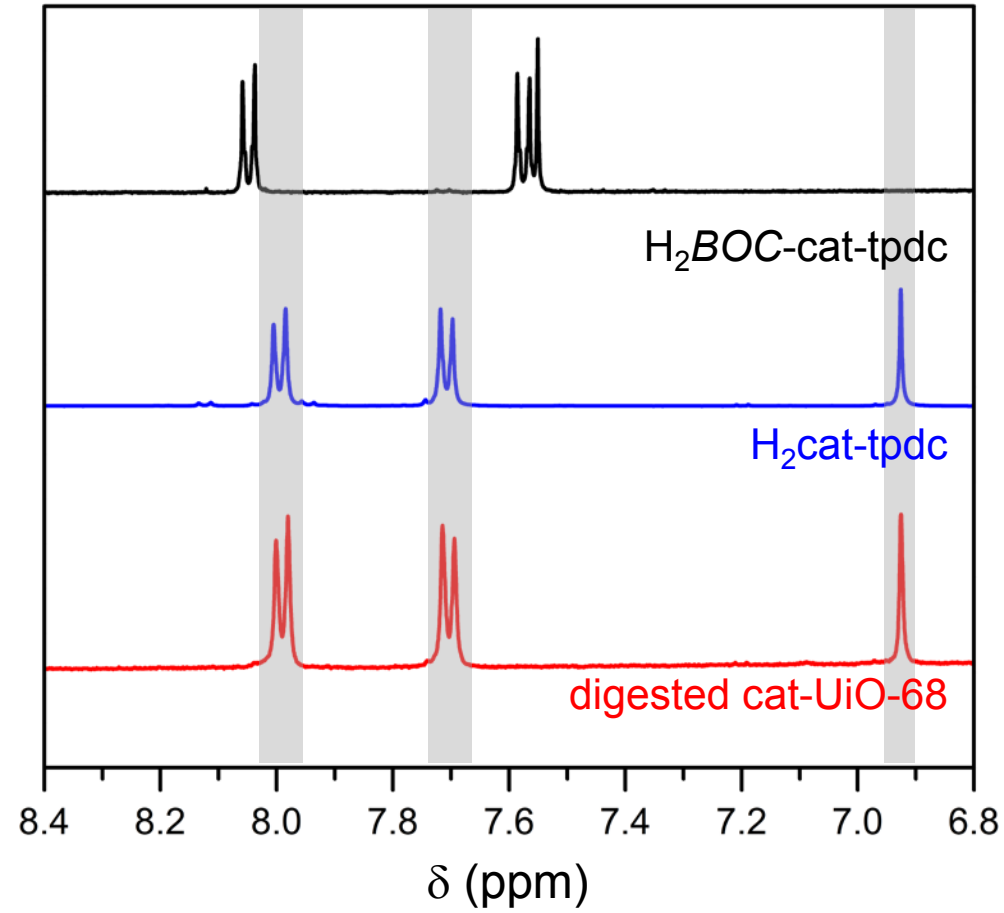
Accomplishments: Cyclic Carbonate is the Likely Side Product

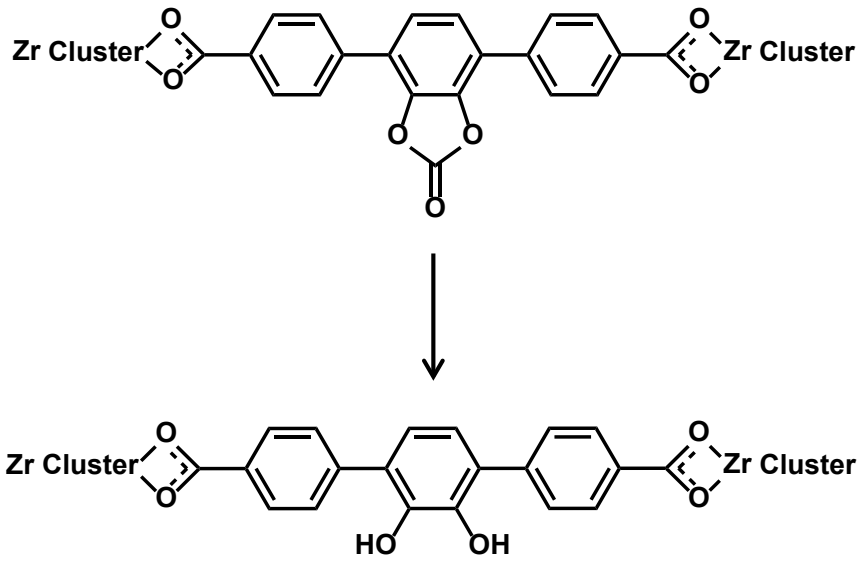




- High energy carbonyl stretch suggests cyclic carbonate
- Ligand with cyclic carbonate was directly synthesized and confirmed hypothesis *via* NMR and infrared spectroscopy

Accomplishments: Hydrolysis of *BOC* in Diglyme Gives Free Catechol Groups

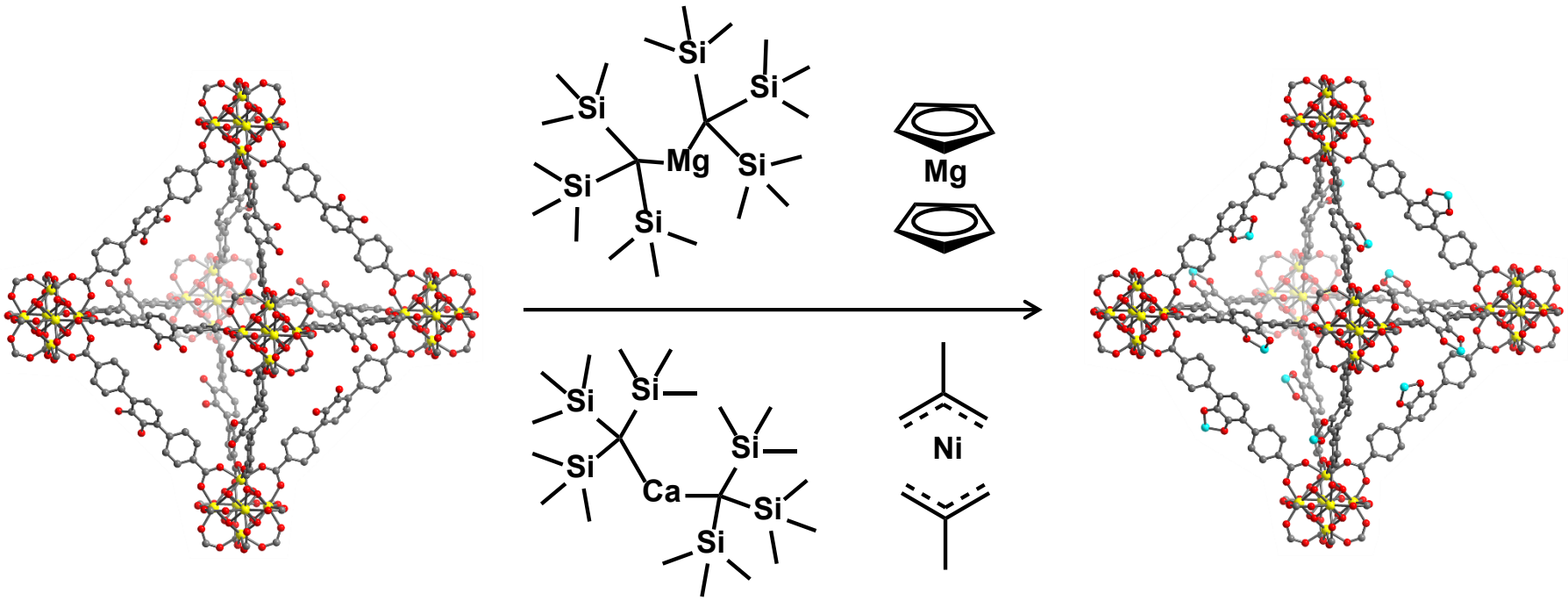




- Hydrolysis in diglyme affords free catechol groups.
- Langmuir surface area of 3790 m^2/g is expected based on large pores; similar to base UiO-68 (4170 m^2/g).

Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc.* **2008**, *130*, 13850.

Proposed Future Work: Cat-UiO-68 Future Directions



- With a fully characterized free catechol MOF, metallation attempts are now underway.
- A variety of low-coordinate metal precursors have been synthesized to use in metallation reactions of the cat-UiO-68.

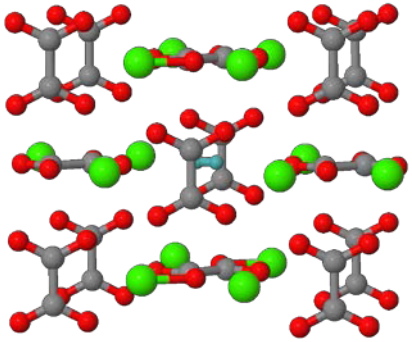
Any proposed future work is subject to change based on funding levels

Accomplishments: Modeling H_2 Binding in Calcium Oxalate

HySCORE

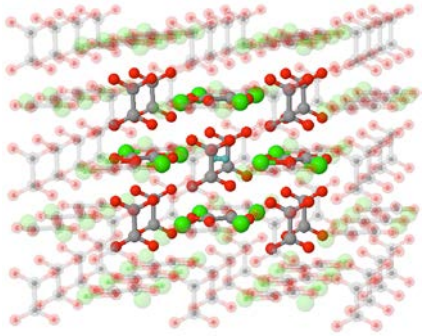
- Collaboration with Tom Gennett's group at NREL, which has experimentally characterized H_2 uptake in calcium oxalate crystals
- We have computationally identified the binding site and computed interaction interaction energy
- Non-specific H_2 interactions with oxalate framework; dispersion-dominated

Vacuum embedding model



ΔE_{ads} = -24.2 kJ mol^{-1}

Charge embedding model



ΔE_{ads} = -26.1 kJ mol^{-1}

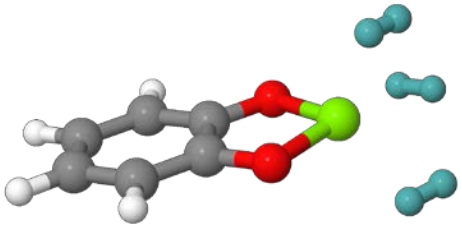
All calculations were done using ωB97M-V/ def2-TZVPD/def2-TZVP at ωB97M-V/6-31G* optimized geometries

- Further work includes decomposition of interaction energy into chemically meaningful components
- We also intend to develop a theoretical framework to treat the extended system of the crystal – can also be used to model MOFs

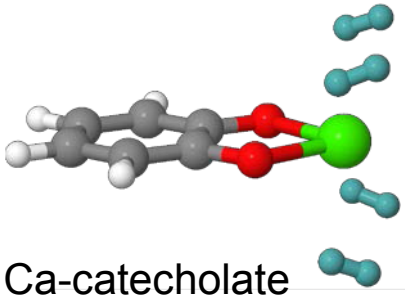
Accomplishments: Metallated Catecholates Bind Multiple H_2

HySCORE

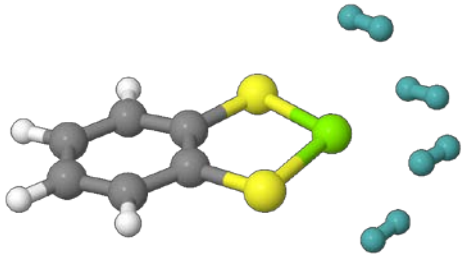
- A post-synthetic modification proposed to enhance the capacity of MOFs
- Ca-catecholates, Mg-catecholates and thio-catecholates investigated



Mg-catecholate



Ca-catecholate



Mg-thiocatecholate

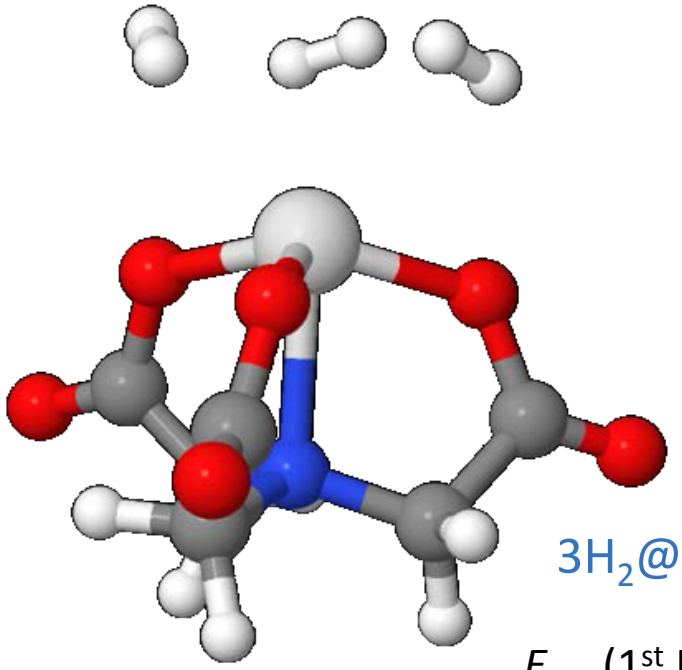
Adsorption energies* for the reactions
cat-M-(*n*-1)H_2 + H_2 → cat-M-(*n*)H_2

n	Mg-cat	Ca-cat	Mg-tcat
1	–23.8	–15.9	–18.7
2	–22.2	–15.5	–12.8
3	–15.4	–15.1	–7.4
4		–14.7	–8.4

All values are in kJ mol^{-1} and calculated at ωB97M-V/def2-QZVPD at ωB97M-V/def2-TZVPD optimized geometries.

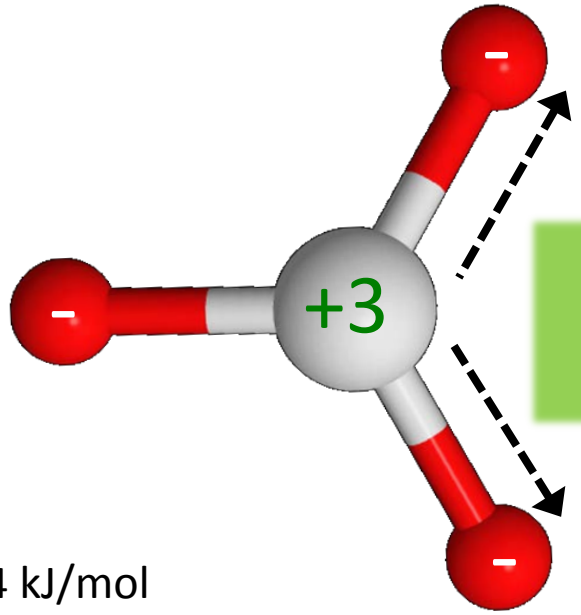
Tsivion, E.; Veccham, S. P.; Head-Gordon, M. *ChemPhysChem* 2017, *18*, 184

Accomplishments: Multiple H_2 Adsorbed Computationally with Sc^{3+}



$3H_2$@Sc-NTA

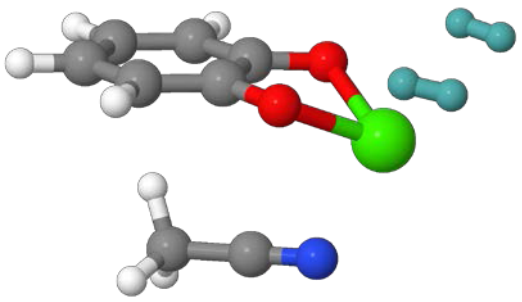
Top view



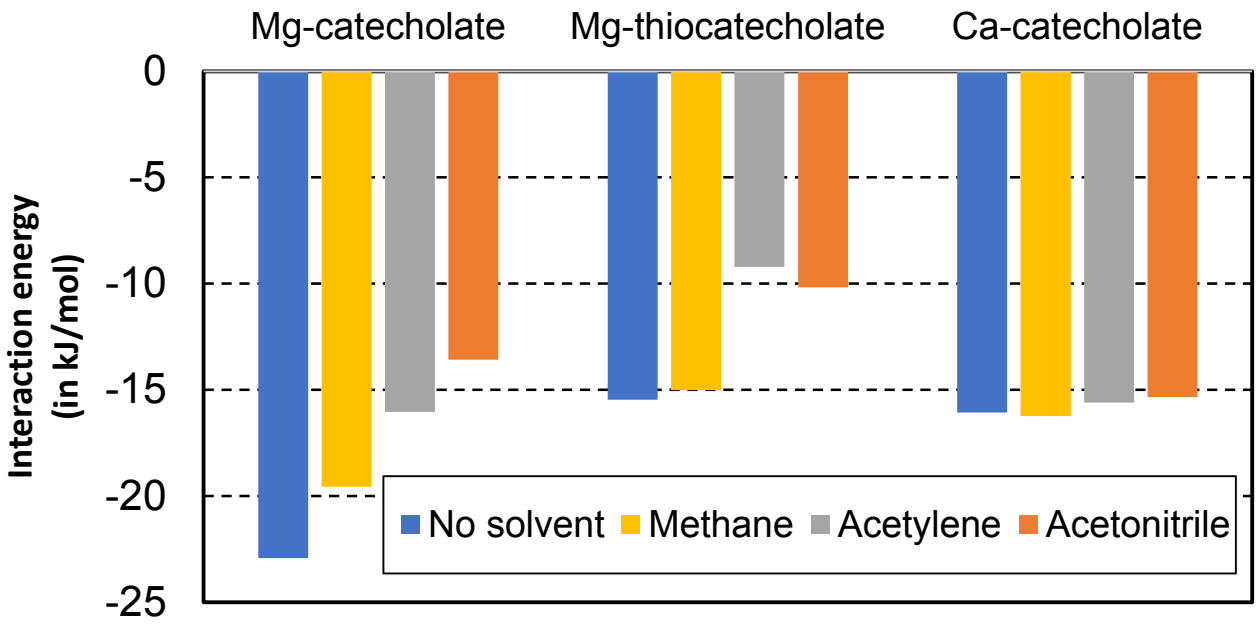
Strong local quadrupole moments

E_{ads} (1st H_2) = −20.4 kJ/mol
E_{ads} (2nd H_2) = −16.0 kJ/mol
E_{ads} (3rd H_2) = −14.6 kJ/mol

Accomplishments: Solvent Effects on H_2 Binding Energy

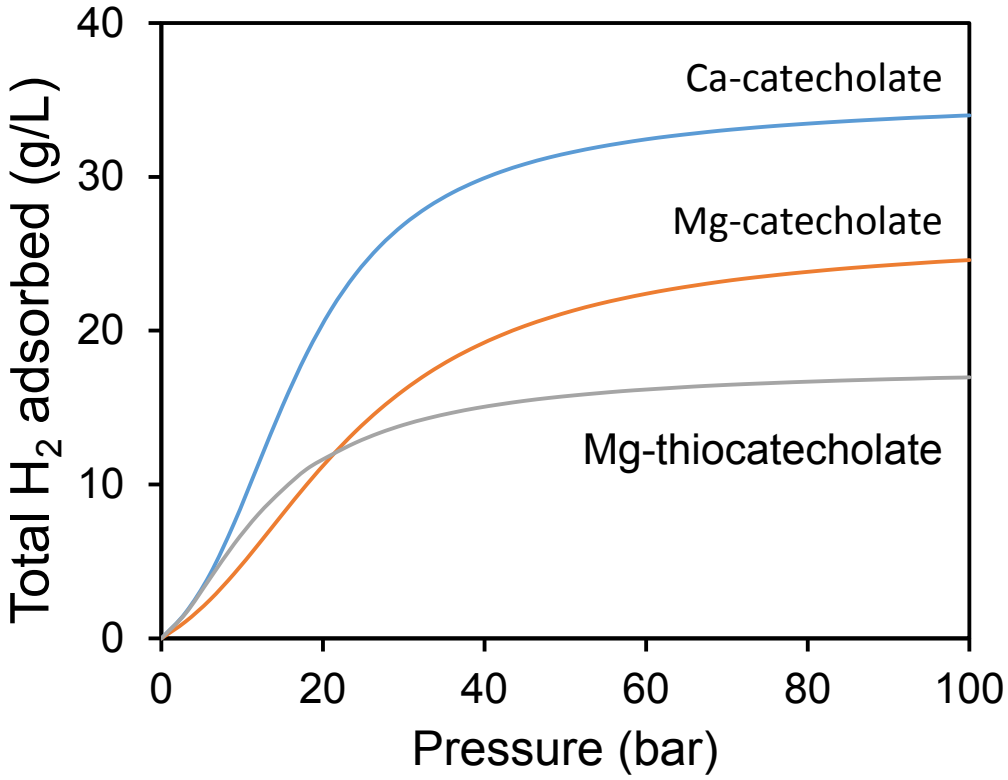


Ca-catecholate binding to 2 H_2 in the presence of acetonitrile



- Interaction energy typically decreases upon solvent binding
- Calcium catecholate is predicted to be an exception
- Maximum number of H_2 bound to the metal decreases by 1 or 2 upon solvent binding.

Accomplishments: Usable Capacity Estimate for Metallated UiO-66

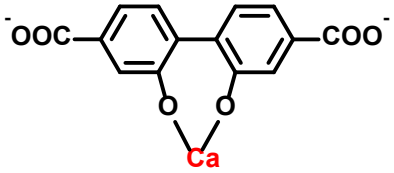
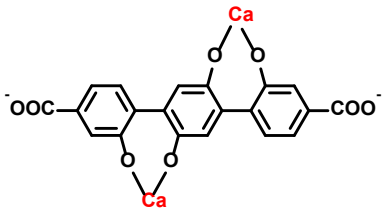
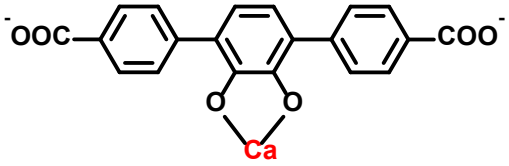
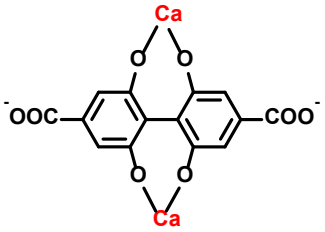
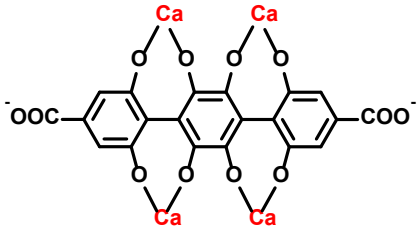
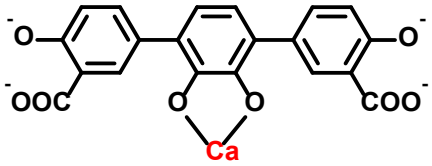


- Unmodified MOF contributes about 10 g/L.
- Ca-metallation adds about 30g/L
- Ca-catecholate has the potential to achieve 40 g/L total capacity based on single crystal density.

	Ca-cat	Mg-cat	Mg-tcat	2020 Target
Usable Capacity	30.3 g/L	22.4 g/L	13.4 g/L	40 g/L

Accomplishments: Predicted Capacities Upon Insertion of Ca^{2+}

HySCORE

UiO-67-Ca	UiO-68-Ca_2	Ca-cat-UiO-68
4.5 wt%, 41 g/L	6.6 wt%, 47 g/L	6.2 wt%, 38 g/L
		
UiO-67-Ca_2	**UiO-68-Ca_4**	**Ca-Mg_2(cat-dotpdc)**
5.2 wt%, 56 g/L	7.5 wt%, 64 g/L	7.1 wt%, 38 g/L
		

- Predicted total capacities (based on single crystal densities) with 4 H_2/Ca^{2+} and H_2 packing in pores of Ni_2(*m*-dobdc)
- These compounds will provide proof of principle that multiple H_2 on metal centers can lead to high storage capacities

Responses to Previous Year Reviewers' Comments

HySCORE

FY16 Reviewer Comment	FY17 Response to Comment
Obtaining either [MOFs with multiple open sites per metal or with a higher density of metals] is a serious challenge, requiring an approach and material system(s) that have not yet been identified.	We believe that we have outlined in this talk our approach to both of these solutions and how each can significantly boost the volumetric capacity of materials. Our approach significantly
It was not clarified how much time will be available for the DRIFTS instrument to perform those critical measurements on hydrogen binding energies for other research groups investigating hydrogen adsorption mechanisms.	Access to measurements with the DRIFTS instrument is available to the wider hydrogen storage research community for validation of key materials, pending approval of our program managers. As stated in our milestones, time is available for at least two external samples to be thoroughly investigated each year.

Remaining Challenges and Barriers

HySCORE

- Insertion of catecholate-bound metal cations remains a challenge
- Strategies being developed between theory and experimental collaborators are designed to help desolvate such metal cations in MOFs
- Experimental demonstration that more than two H_2 molecules can be adsorbed at a single metal site is a key current challenge
- Computational tools are well-poised to accurately explore binding energies of actual and proposed binding sites. Accurate calculation of binding entropies is challenging.

Any proposed future work is subject to change based on funding levels

Proposed Future Work

HySCORE

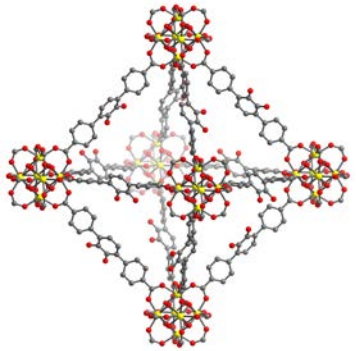
- Synthesize and measure H_2 adsorption on new MOFs containing a high density of metal cations, including more compact variants of M_2(dobdc).
- Test metalation and desolvation conditions for the catechol-containing frameworks in partnership with computation.
- Validate hypothesis that more than two H_2 molecules can adsorb at a single metal site.
- Computational exploration of new metalation sites – experimentally proposed, as well as new designs.
- Fully validate cryogenic capabilities in *in situ* infrared spectrometer and investigate key new samples.

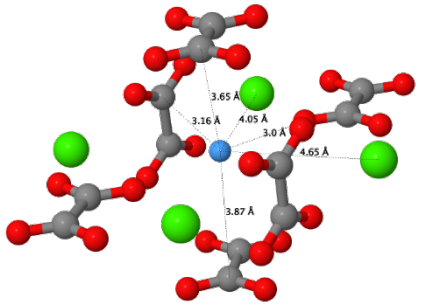
Any proposed future work is subject to change based on funding levels

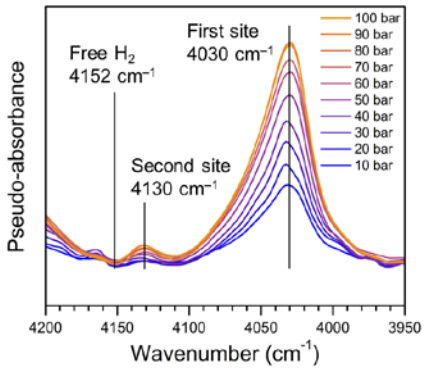
Summary

HySCORE

- Synthesized *BOC*-cat-UiO-68 with high surface area, high crystallinity, and in good yield.
- Extensively studied the deprotection of *BOC*-cat-UiO-68 to expose catechols for metallation in cat-UiO-68.
- Progress towards synthesizing and metallating and several other MOFs for use as hydrogen storage materials.
- Performed theory calculations to understand both the desolvation process of metals bound to catechols and the binding of H_2 in calcium oxalate.
- Installed *in situ* infrared spectrometer and obtained initial positive results in system.







Summary (Synthesis and Modeling)

HySCORE

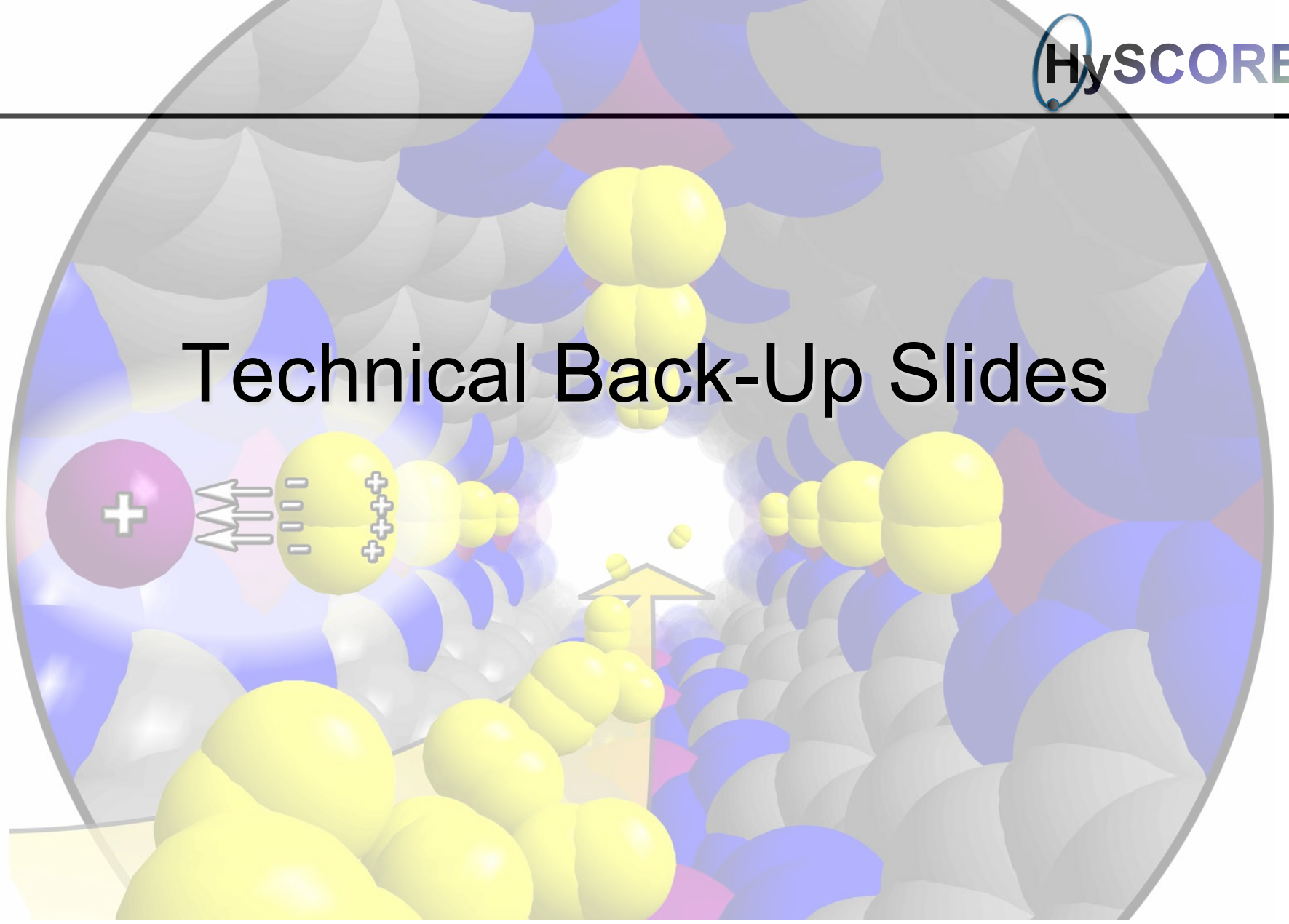
Milestone	% complete
FY16 Q4 Go/No-go: Demonstrate the ability to bind two H_2 molecules to one metal center in a metal-organic framework, porous aromatic framework, or carbon-based material.	**100%**
FY17 Q2: Synthesize a framework, aerogel, or polymeric material exhibiting a total H_2 storage capacity of at least 30 g/L at temperatures above 100 K and <150 bar.	**100%**
FY17 Q3: Demonstrate computational accuracy by showing that the calculated capacity for a MOF, PAF, or carbon-based material with multiple H_2 molecules bound per metal is within 15% of the experimental capacity.	75%

Summary (DRIFTS)

HySCORE

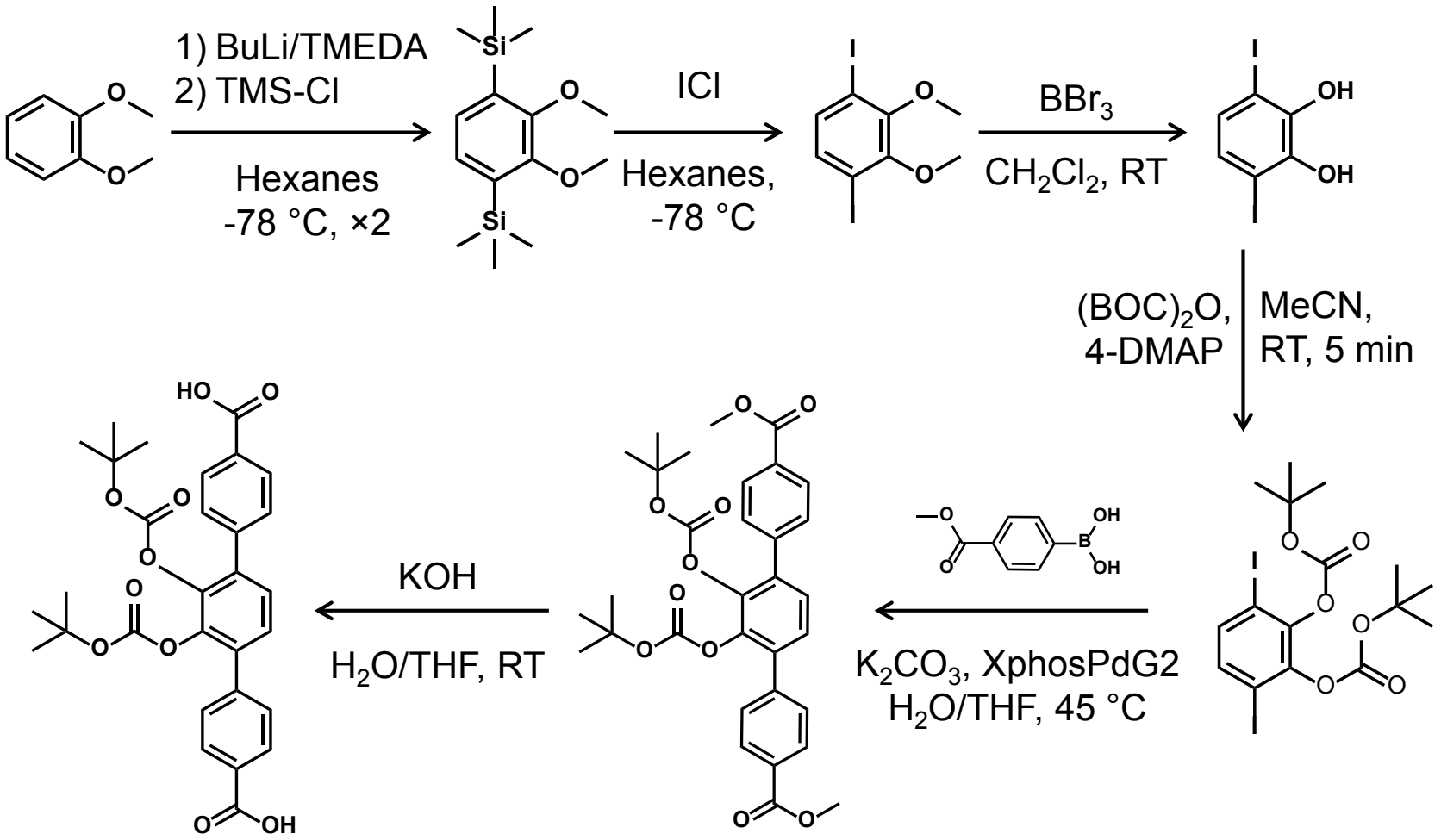
Milestone	% complete
FY16 Q3: Order DRIFTS instrument that will be best and most functional for the desired in situ H_2-dosed experiments based on experience testing several similar instruments.	**100%**
FY16 Q4: Initiate installation of the DRIFTS instrument.	**100%**
FY17 Q1: Demonstrate that the DRIFTS instrument is operating with a resolution of 10 cm^{-1} by measuring spectra for a mutually agreed-upon sorbent standard under 1 bar H_2 at 298 K and comparing with accepted published data.	**100%**
FY17 Q2: Demonstrate that the DRIFTS instrument is operating at pressures up to 50 bar of H_2 and comparing with accepted published data.	**100%**
FY17 Q3: Demonstrate a) that the DRIFTS instrument is operating with a resolution of 10 cm^{-1} by measuring spectra for a mutually agreed upon sorbent standard at 1 bar H_2 in the temperature range 77–373 K and b) the ability to determine H_2 adsorption enthalpies on a mutually agreed upon sorbent standard from variable-temperature spectra collected on the DRIFTS spectrometer to within 10% of the accepted values.	50%
FY17 Q4: Submit DOE report and/or peer reviewed manuscript on the DRIFTS instrument, its capabilities, and the application of the system to hydrogen storage materials characterization.	10%

Technical Back-Up Slides

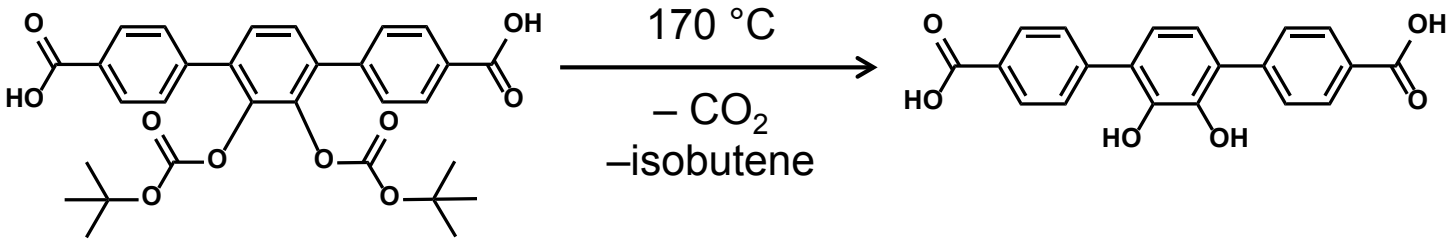


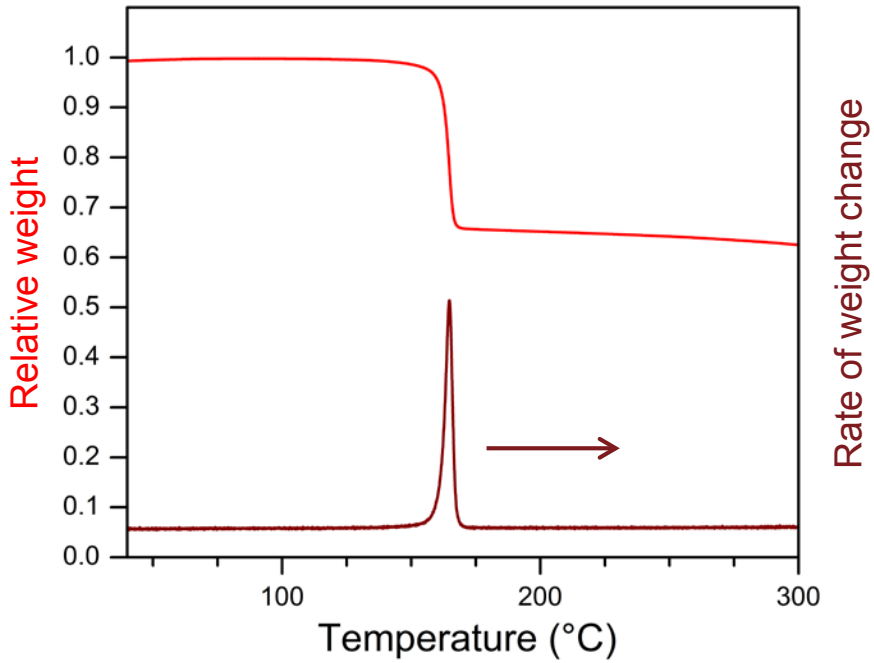
Synthesis of H_2(*BOC*-cat-tpdc)

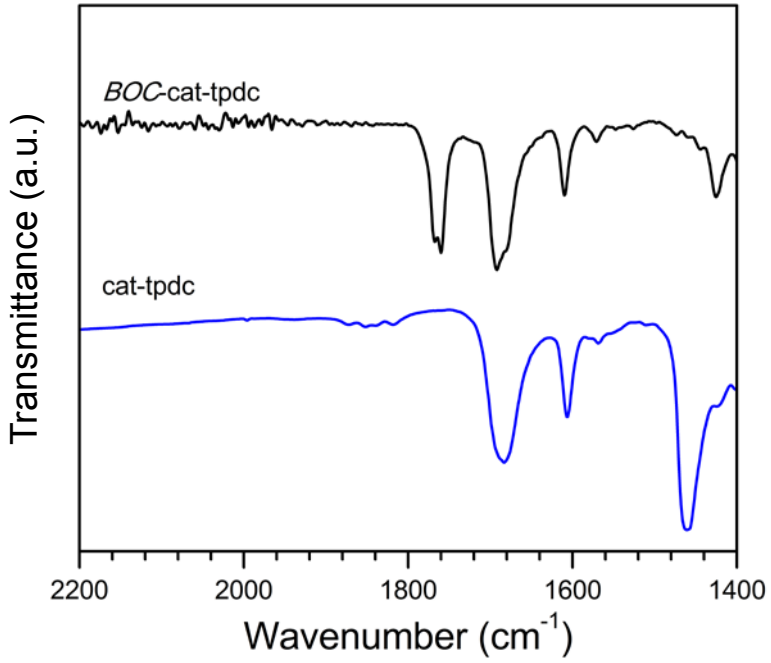
HySCORE



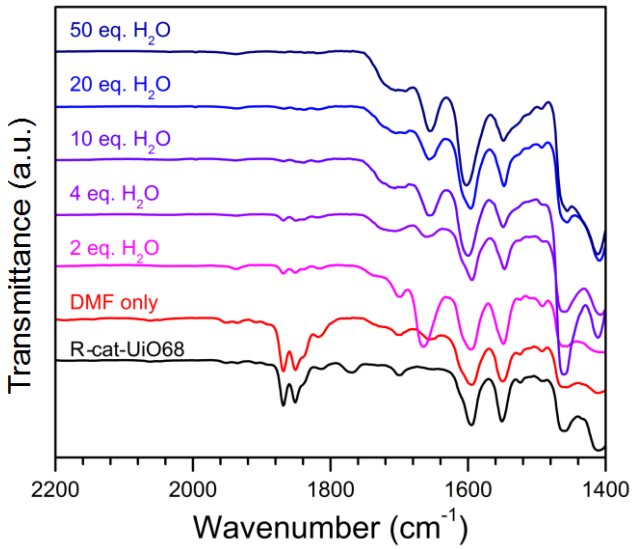
Thermal Deprotection was Successfully Performed on H_2(*BOC*-cat-tpdc) Ligand

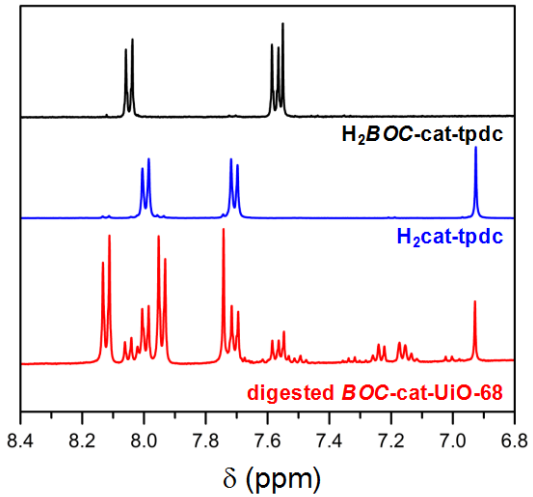


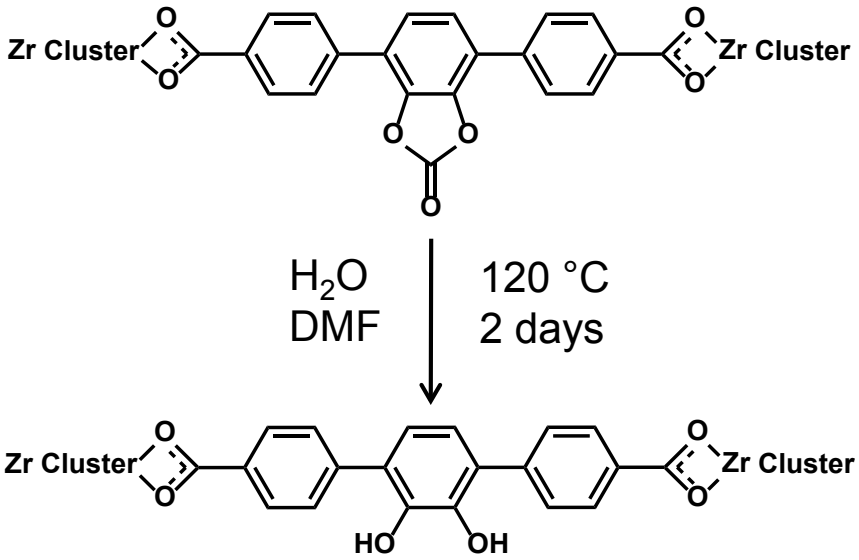




Hydrolysis of Partially Deprotected Framework

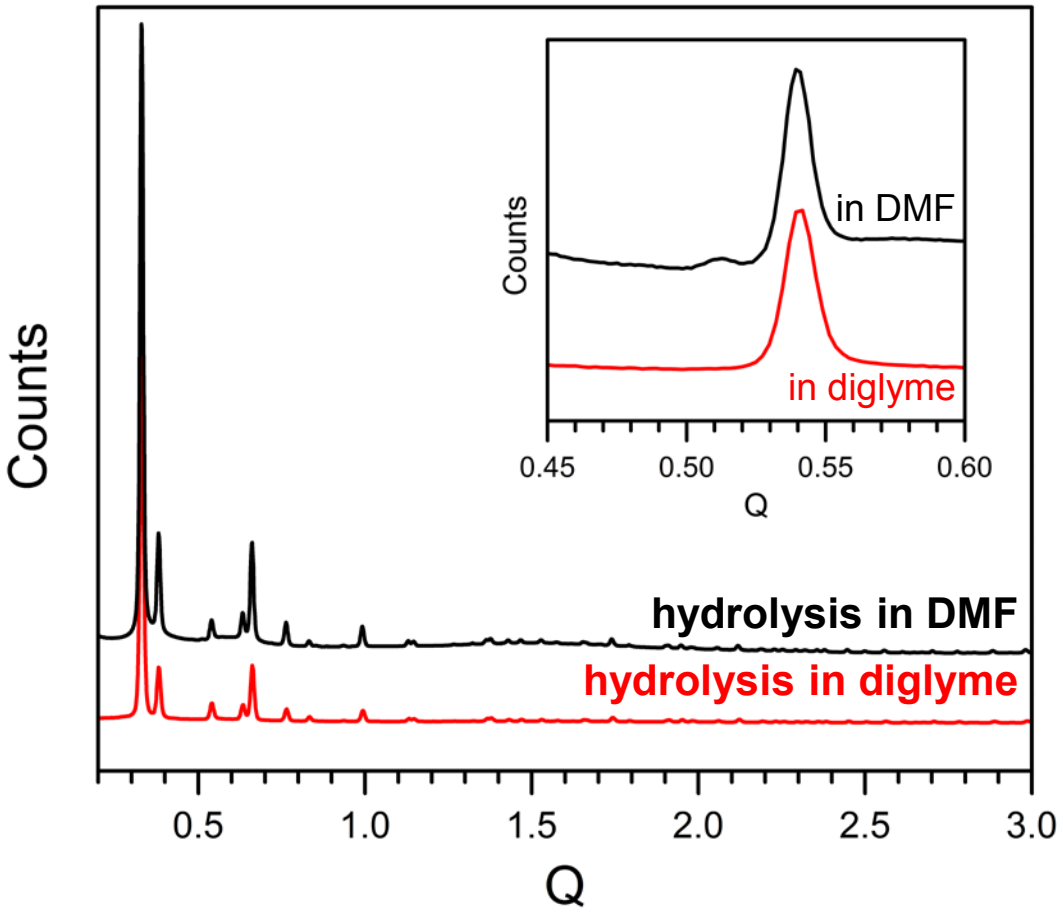






- Cyclic carbonate group was successfully hydrolyzed in DMF at 120 °C.
- Surface area decreased to 1940 m^2/g using this deprotection method.

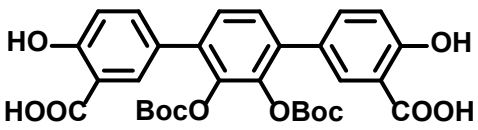
Phase-Pure cat-UiO-68



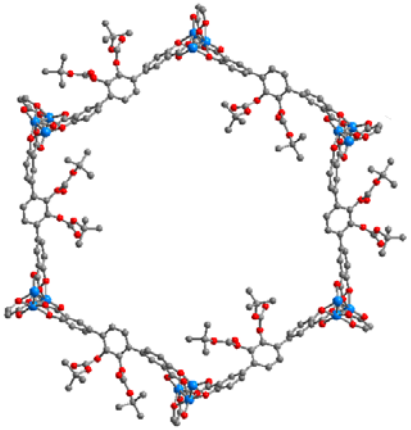
Langmuir SA (m^2/g)	
Hydrolysis in DMF	1940
Hydrolysis in diglyme	3790

Phase impurity is no longer present and surface area is substantially increased using diglyme.

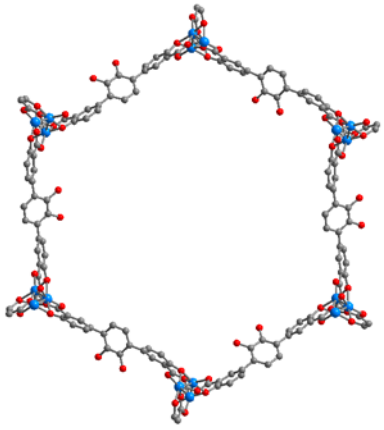
Accomplishments: Synthesis of Mg_2(BOC-dotpdc)



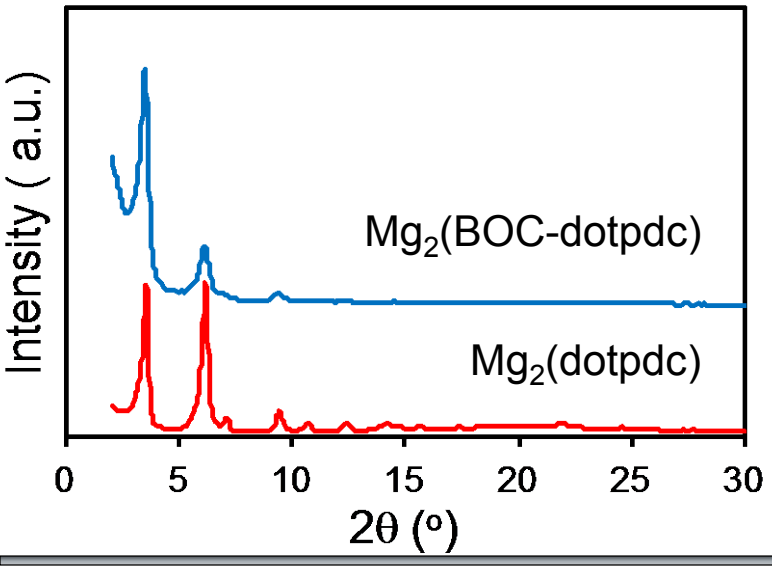
$Mg(NO_3)_2$ → Deprotection →



Mg_2(BOC-dotpdc)
(modeled structure)



Mg_2(cat-dotpdc)
(modeled structure)
Langmuir SA = 5070 m^2/g

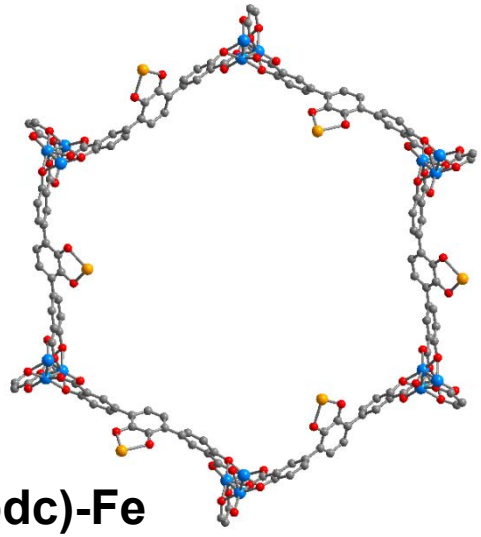


- MOF synthesis with BOC ligand is produces the intended structure type.
- Infrared spectroscopy confirms presence of BOC in crystalline material.
- Full BOC deprotection consistent with high resulting surface area.
- Mg_2(cat-dotpdc) prepared using non-protected ligand resulted in a similarly high Langmuir surface area of 5330 m^2/g.

Accomplishments: Mg_2(cat-dotpdc) Metallation with $Fe_2(Mes)_4$

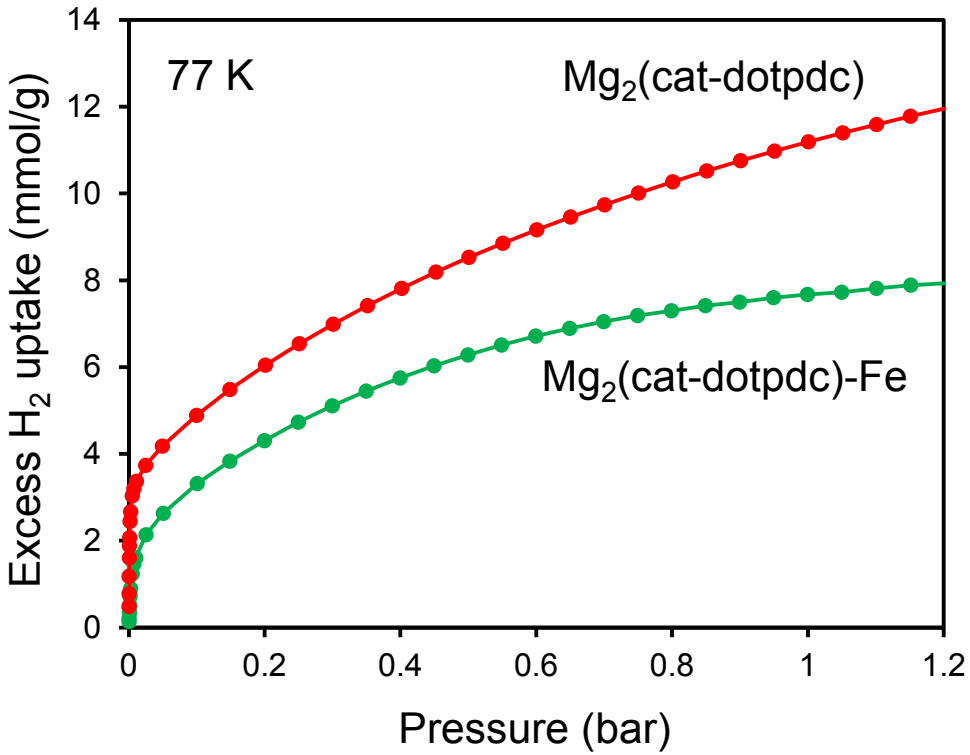
HySCORE

Mg_2(cat-dotpdc) → tetramesityldiiron, $Fe_2(Mes)_4$



Mg_2(cat-dotpdc)-Fe
(Modeled structure)

Langmuir SA: 3660 (m^2 g^{-1})
ICP analysis: Fe/Mg = 0.21



Metallation attempts with several different metal sources have thus far all resulted in reduced H_2 uptake